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Synthesis and Study of Metallonitride Complexes and Polymers

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13. ABSTRACT (Maximum 200 words)

The synthesis and chemistry of compounds in which two transition metal centers are bridged by a single nitrogen atom, the bridging nitride ligand, has been investigated. These studies have focused on understanding the chemical and physical properties of the M(N)M unit in order to explore its use as a building block for new transition metal-containing polymers. The approach to this chemistry has involved parallel exploration of molecular nitride-bridged species, which serve as model systems for developing the chemistry of these compounds, and of extended structures incorporating metal-nitrogen-metal linkages. Supporting studies on the preparation and reactivity of silylimido precursor compounds, which are used in the synthetic route to nitride-bridged structures, have also been performed.

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COMPLETED PROJECT SUMMARY

TITLE: Synthesis and Study of Metallonitride Complexes and Polymers

PRINCIPAL INVESTIGATOR: Professor Nancy M. Doherty
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PUBLICATIONS:

"Vanadium Nitride Linear Chain Polymers and Monomers. Synthesis and Structures of $[V(\mu-N)Cl_2(py)_2]_\infty$ and $V(N)Cl_2(quin)_2$," S. C. Critchlow, M. E. Lerchen, R. C. Smith, and N. M. Doherty, *J. Am. Chem. Soc.*, 1988, 110, 8071.

"Synthesis of Molybdenum and Tungsten Silylimido Complexes. Structure of a Five-Coordinate Bis(silylimido) Complex," J. D. Lichtenhan, S. C. Critchlow, and N. M. Doherty, *Inorg. Chem.*, 1990, 29, 439.

"Synthesis of Vanadium, Niobium, and Tantalum Silylimido Complexes and Reactivity of Their Nitrogen-Silicon Bonds," C. M. Jones, M. E. Lerchen, C. J. Church, B. M. Schomber, and N. M. Doherty, *Inorg. Chem.*, 1990, 29, 1679.

"Transition-Metal Fluoro Complexes Containing Carbonyl, Phosphine, Arsine, or Stibine Ligands," N. M. Doherty and N. W. Hoffman, *Chem. Rev.*, 1991, 91, XXXX.

Five additional manuscripts are in preparation.

ABSTRACT OF OBJECTIVES AND ACCOMPLISHMENTS:

This project has focused on investigation of the synthesis and chemistry of compounds in which two transition metal centers are bridged by a single nitrogen atom, the bridging nitride ligand. The research is directed at understanding the chemical and physical properties of the M(N)M unit in order to explore its use as a building block for new transition metal-containing polymers. Our approach has involved the parallel exploration of molecular nitride-bridged species, which serve as model systems for developing the chemistry of these compounds, and of extended structures incorporating metal-nitrogen-metal linkages. Inorganic polymers in which transition

metal atoms are incorporated into the structural backbone are anticipated to be important new materials with a variety of desirable properties, however study of these systems is currently limited by the scarcity of methods available for their synthesis. Our work has aimed at using and understanding a simple condensation reaction between silylimido and halide (especially fluoride) ligands that we have discovered for the preparation of metallonitride complexes and polymers.

Using this chemistry, we have prepared a series of new vanadium-rhenium, -rhodium, -iridium, and iridium-iridium nitride-bridged complexes. Spectroscopic, physicochemical, and reactivity studies of these species, as well as X-ray structural studies of selected compounds, have established that these systems possess asymmetric linear nitride bridges with stable bonds between the nitride ligand and two very different metal centers. These studies have allowed us to develop a detailed understanding of the influence of changes in the metal, its oxidation state, and its ligands on the structure and stability of the nitride bridge.

A key feature of the condensation reaction is its potential for the preparation of polymeric metallonitrides from starting materials having the silylimido and halide ligands on the same metal center. Using this reaction, we have prepared new linear chain polymers based on a vanadium-nitride backbone and containing pyridine ligands. The vanadium nitride polymers have remarkable stability as crystalline solid state compounds. X-ray diffraction studies reveal the detailed structure of the pyridine derivative which is a linear chain metallonitride polymer composed of six-coordinate vanadium centers joined by alternating short and very long V-N bonds. Comparison of the solid state structures and solution behaviors of a series of these derivatives demonstrates that a critical feature in determining the stability of the nitride-bridged structures is π -stacking interactions between pairs of pyridine ligands on neighboring chains.

The rapid self-assembly of this highly ordered polymeric structure in quantitative yield is striking. In order to learn how to extend this chemistry to the synthesis of other metallonitride polymers, we have used reactivity and kinetic studies to address the mechanism of the condensation/polymerization reaction. Mechanistic modelling has demonstrated that both intermolecular condensation of vanadium silylimido chloride derivatives and oligomerization of vanadium nitrido monomers can yield the nitride-bridged linear chain complex.

In order to explore the scope of the condensation reaction for the synthesis of a variety of nitride-bridged molecular compounds and extended structures, we need to be able to vary the starting silylimido derivative. Silylimido compounds are rather rare, therefore we have focused effort on developing methods for their preparation. We have synthesized a family of niobium and tantalum silylimido complexes using hexamethyldisilazane as the source of the trimethylsilylimido group and a series of molybdenum and tungsten silylimido derivatives by the addition of trimethylsilylazide to oxidizable molybdenum and tungsten complexes, and have explored the reactivity of these compounds.

Overall, our efforts to use a molecular approach toward transition metal-containing polymers have progressed well. Specifically, we have learned how to synthesize a range of silylimido compounds, developed a reaction based on condensation of silylimido and halide ligands for the synthesis of nitride-bridged bimetallic complexes, and applied this chemistry to the preparation of polymeric vanadium nitride linear chain compounds. Furthermore, from our studies of these systems a detailed picture of the nitride bridge and its potential for use as a building block for new transition metal-containing polymers is emerging.



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UNIVERSITY OF WASHINGTON
SEATTLE, WASHINGTON 98195

**SYNTHESIS AND STUDY OF METALLONITRIDE COMPLEXES AND
POLYMERS**

Final Report for AFOSR-87-0362

For Period: September 15, 1987 – August 30, 1990

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Date of Report: February 20, 1990

INTRODUCTION

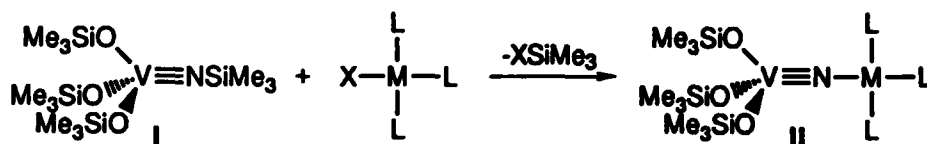
We have been investigating the synthesis and chemistry of compounds in which two transition metal centers are bridged by a single nitrogen atom, the bridging nitride ligand. This research is focused on understanding the chemical and physical properties of the $M(N)M$ unit in order to explore its use as a building block for new transition metal-containing polymers. Our approach has involved the parallel exploration of molecular nitride-bridged species, which serve as model systems for developing the chemistry of these compounds, and of extended structures incorporating metal-nitrogen-metal linkages. Inorganic polymers in which transition metal atoms are incorporated into the structural backbone are anticipated to be important new materials with a variety of desirable properties, however study of these systems is currently limited by the scarcity of methods available for their synthesis. Our work has aimed at using and understanding a simple condensation reaction that we have discovered for the preparation of metallonitride complexes and polymers.

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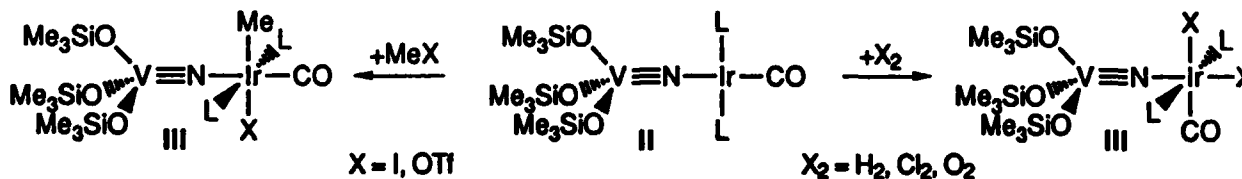
RESEARCH ACCOMPLISHMENTS

Our AFOSR-supported research on transition metal compounds with bridging nitride ligands has focused on three aspects of this chemistry: (a) synthesis and study of bimetallic nitride-bridged model compounds, (b) formation and structure of linear chain metallonitride polymers, and (c) preparation and reactivity of silylimido precursor compounds. Our most significant results in these areas are summarized below.

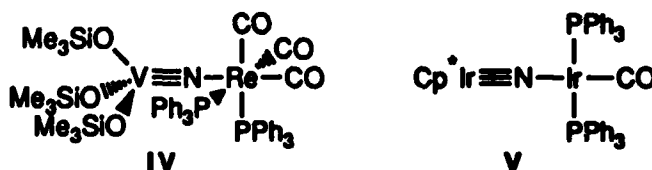
Bimetallic nitride-bridged model compounds. We have developed a synthetic route to nitride-bridged complexes based on a simple condensation reaction between silylimido and halide ligands. Using this chemistry, we have prepared a series of new nitride-bridged vanadium-rhodium and -iridium complexes (II), isolated in high yield from the reaction of I with square planar group VIII metal fluorides (paper #6).



Analogous reactions of I with rhodium and iridium methoxide and acetate derivatives also produce II. These air-sensitive compounds are readily characterized by standard techniques including NMR (^1H , ^{13}C , ^{31}P , ^{51}V) spectrometry, IR spectroscopy, and elemental analysis. The iridium compounds undergo a number of clean oxidative addition reactions at the group VIII metal center, yielding new nitride-bridged derivatives (III) in which an octahedral iridium(III) is linked to vanadium(V) via the nitride ligand (paper #6).



We have successfully extended the condensation reaction to coordinatively saturated metal fluorides and to late metal silylimido complexes, synthesizing vanadium-rhenium (IV) (paper #5) and iridium-iridium (V) (paper #9) nitride-bridged compounds.

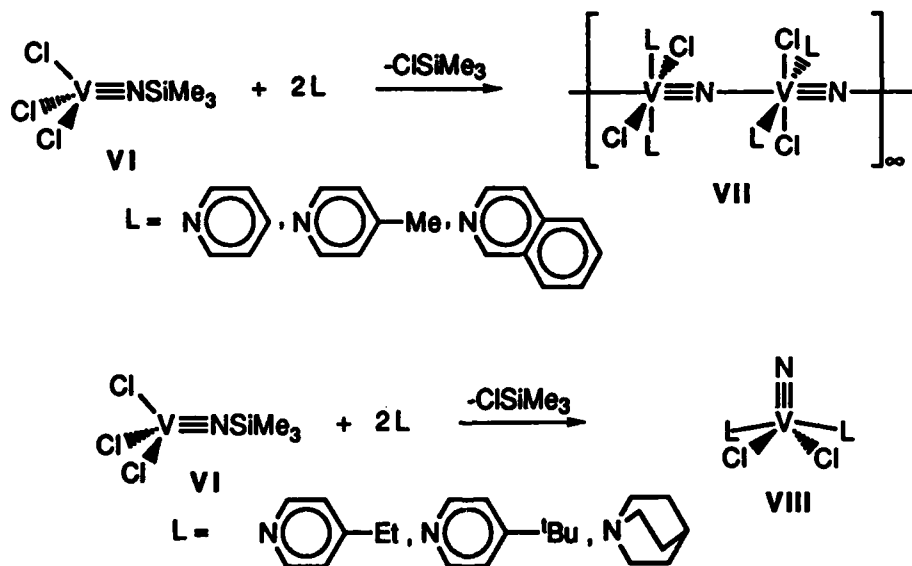


Synthesis of compounds IV-V is significant because it demonstrates the generality of our method for formation of the nitride bridge and because it has allowed us entry into new nitride-bridged systems for detailed study.

Spectroscopic, physicochemical, and reactivity studies of II-V, as well as X-ray structural studies of selected compounds, have established that these systems possess asymmetric linear nitride bridges with stable bonds between the nitride ligand and two very different metal centers, and have allowed us to develop a detailed understanding of the influence of changes in the metal, its oxidation state, and its ligands on the structure and stability of the nitride bridge.

Linear chain metallonitride polymers. A key feature of the condensation reaction is its potential for the preparation of polymeric metallonitrides from starting materials having the silylimido and halide ligands on the same metal center. Using this reaction, we have prepared new linear chain polymers based on a vanadium-nitride backbone.

By substitution of the siloxide ligands of I we have synthesized a vanadium(I) silylimido derivative possessing reactive metal-chlorine bonds (VI). Compound VI undergoes rapid elimination of chlorotrimethylsilane on addition of two equivalents of pyridine or other nitrogen bases producing vanadium(V) nitrido ligands in high yield. Depending on the identity of the ancillary ligands, either polymeric nitride-bridged compounds (VII) or monomeric complexes with terminal nitride ligands (VIII) are formed (paper #1).



Compounds VII and VIII are among the very first examples of vanadium nitrido derivatives known.

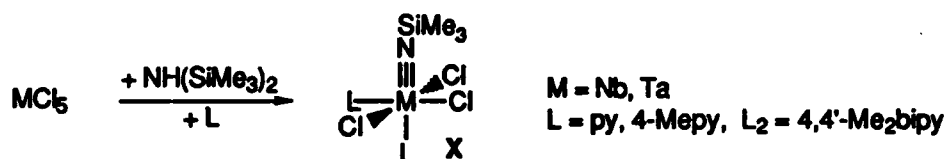
The vanadium nitride polymers (VII) have remarkable stability as crystalline solid state compounds. X-ray diffraction studies reveal the detailed structure of the pyridine derivative which is a linear chain metallonitride polymer composed of six-coordinate vanadium centers joined by alternating short and very long V-N bonds. Comparison of the solid state structures and solution behaviors of VII and VIII demonstrates that a critical feature in determining the stability of the

nitride-bridged structures in VII is π -stacking interactions between pairs of pyridine ligands on neighboring $[V(\mu-N)Cl_2L_2]_{\infty}$ chains (paper #1).

The rapid self-assembly of this highly ordered polymeric structure in quantitative yield is striking. In order to learn how to extend this chemistry to the synthesis of other metallonitride polymers, we have used reactivity and kinetic studies to address the mechanism of the condensation/polymerization reaction. We have shown that a highly reactive intermediate, $V(NSiMe_3)Cl_3L_2$ (IX) can be isolated and observed spectroscopically at low temperatures and is the major vanadium-containing species present during the condensation reactions. Compound IX reacts to produce either polymeric VII or vanadium nitride monomers, depending on the reaction conditions. Mechanistic modelling of the disappearance of IX has demonstrated that both intermolecular condensation of IX and oligomerization of monomers can yield the nitride-bridged linear chain complex (paper #8).

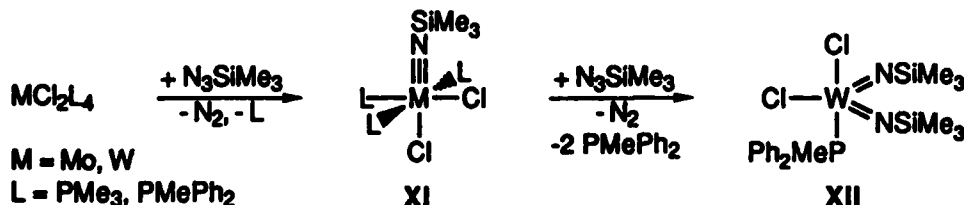
Silylimido precursor compounds. In order to explore the scope of the condensation reaction for the synthesis of a variety of nitride-bridged molecular compounds and extended structures, we need to be able to vary the starting silylimido derivative. Silylimido compounds are rather rare, therefore we have focused effort on developing methods for their preparation.

We have synthesized a family of niobium (V) and tantalum (V) silylimido complexes (X) using hexamethyldisilazane, $NH(SiMe_3)_2$, as the source of the trimethylsilylimido group (paper #3).

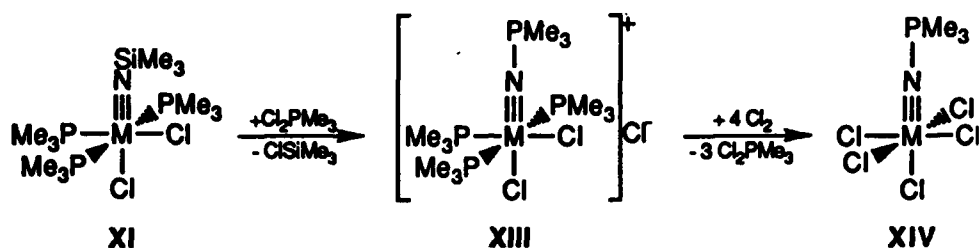


These compounds are closely related to VI and analogous to its pyridine ligand adducts IX. Surprisingly, however, compounds X require significantly more forcing conditions for elimination of chlorotrimethylsilane and do not cleanly produce nitride products.

We have also prepared a series of molybdenum(IV) and tungsten(IV) mono(silylimido) (XI) and tungsten(VI) bis(silylimido) (XII) derivatives by the addition of trimethylsilylazide to oxidizable molybdenum and tungsten complexes (paper #2).



In contrast to the niobium and tantalum compounds, XI-XII possess highly reactive silylimido ligands. Of particular interest are their clean reactions with chlorine and phosphine dichlorides to yield phosphiniminato compounds (XIII-XIV) (paper #7).



These remarkable transformations are important not only to our understanding of the reactivity of the silylimido ligand, which has been the nitrogen-containing building block for our synthesis of nitride-bridged compounds, but also because they provide us with reactive nitrogen-phosphorus bonds in compounds which may also serve as good precursors to nitride-bridged systems.

Summary. Our efforts to use a molecular approach toward understanding transition metal-containing polymers have progressed well. Specifically, we have learned how to synthesize a range of silylimido compounds, developed a reaction based on condensation of silylimido and halide ligands for the synthesis of nitride-bridged bimetallic complexes, and applied this chemistry to the preparation of polymeric vanadium nitride linear chain compounds. Furthermore, from our studies of these systems a detailed picture of the nitride bridge and its potential for use as a building block for new transition metal-containing polymers is emerging.

PUBLICATIONS ACKNOWLEDGING AFOSR SUPPORT

1. "Vanadium Nitride Linear Chain Polymers and Monomers. Synthesis and Structures of $[\text{V}(\mu\text{-N})\text{Cl}_2(\text{py})_2]_\infty$ and $\text{V}(\text{N})\text{Cl}_2(\text{quin})_2$," S. C. Critchlow, M. E. Lerchen, R. C. Smith, and N. M. Doherty, *J. Am. Chem. Soc.*, 1988, 110, 8071.
2. "Synthesis of Molybdenum and Tungsten Silylimido Complexes. Structure of a Five-Coordinate Bis(silylimido) Complex," J. D. Lichtenhan, S. C. Critchlow, and N. M. Doherty, *Inorg. Chem.*, 1990, 29, 439.
3. "Synthesis of Vanadium, Niobium, and Tantalum Silylimido Complexes and Reactivity of Their Nitrogen-Silicon Bonds," C. M. Jones, M. E. Lerchen, C. J. Church, B. M. Schomber, and N. M. Doherty, *Inorg. Chem.*, 1990, 29, 1679.
4. "Transition-Metal Fluoro Complexes Containing Carbonyl, Phosphine, Arsine, or Stibine Ligands," N. M. Doherty and N. W. Hoffman, accepted for publication in *Chem. Rev.*, 1991.
5. "Synthesis and Reactivity of *trans*- $\text{ReF}(\text{CO})_3(\text{PPh}_3)_2$ and *trans*-(Me_3SiO) $_3\text{V}\equiv\text{N}$ - $\text{Re}(\text{CO})_3$ -(PPh_3) $_2$," N. W. Hoffman, N. Prokopuk, M. J. Robbins, C. M. Jones, and N. M. Doherty, in preparation.

6. "Nature of the Nitride Bridge. Synthesis and Reactivity of Heterobimetallic Nitride-Bridged Complexes," C. M. Jones, D. M.-T. Chan, J. C. Calabrese, and N. M. Doherty, in preparation.
7. "Reactions at Metal-Bound Nitrogen Atoms: Synthesis and Interconversion of Silylimido, Phosphinimino, and Chloroimido Molybdenum and Tungsten Compounds," J. D. Lichtenhan and N. M. Doherty, in preparation.
8. "Mechanism of the Condensation/Polymerization Reaction Forming Vanadium Nitride Linear Chain Compounds," B. M. Schomber and N. M. Doherty, in preparation.
9. "A Novel Nitride-Bridged Compound Containing Two Iridium Centers In Very Different Coordination Environments and Oxidation States," D. S. Glueck, F. J. Hollander, R. G. Bergman, C. M. Jones, S. C. Critchlow, and N. M. Doherty, in preparation.

GRADUATE STUDENTS INVOLVED IN WORK

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Joseph D. Lichtenhan (Ph.D. expected 1991)

Beth M. Schomber (Ph.D. expected 1991)

Kathleen L. Sorensen (Ph.D. expected 1993)